Catalysis at the NSLS: Importance of Oxygen Vacancies in the Behavior of Oxide Catalysts

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Introduction

Metal oxides are widely used as catalysts in environmental chemistry and commercial processes that deal with the conversion of hydrocarbons [1]. Thus, oxide catalysts are useful in the destruction of the SO_2 and NO_x species produced during the combustion of fuels in automobiles, factories and power plants. By preventing the emission of SO_2 and NO_x into the atmosphere, they help to minimize the negative effects of acid rain on the environment [1,2]. Selective oxidation, ammoxidation, and dehydrogenation probably constitute the most important industrial applications of oxide catalysts active for the conversion of hydrocarbons [1]. Each year these processes produce millions of dollars in revenues.

Over the years there has been a considerable interest in obtaining a fundamental understanding of phenomena responsible for the good performance of oxide catalysts [1,3,4]. Part of the problem in explaining the behavior of these systems arises from the fact that they are complex and very difficult to characterize, in many cases containing several interacting phases and a small fraction of active sites [1]. Useful knowledge in this subject can be obtained through synchrotron based techniques, which nowadays allow the detailed study of the interaction of molecules with surfaces (photoemission, x-ray absorption spectroscopy, infrared spectroscopy, etc) or the evolution of catalytic materials under reaction conditions (x-ray diffraction and scattering, extended x-ray absorption fine structure, etc) [5-8]. These techniques become particularly powerful when combined with state-of-the-art density function (DF) calculations [9]. Using such an approach, recent studies carried out at the NSLS (U7A, X7B, X16C, X19A beamlines) have shown the importance of oxygen vacancies in the behavior of oxide catalysts [10-14].

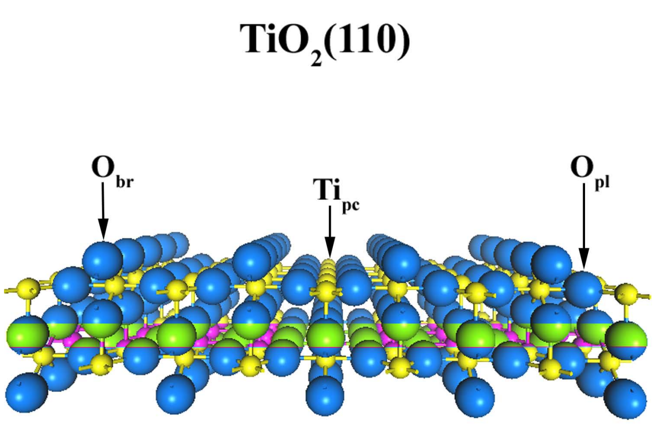

Figure 1. A perfect $TiO_2(110)$ surface. The O atoms are represented as blue spheres, while yellow spheres denote Ti atoms.

DeSOx and DeNOx reactions on Titania

Titania (TiO_2) is used as a catalyst/sorbent for the Claus reaction ($SO_2 + 2H_2S \rightarrow 2H_2O + S_{solid}$) and the destruction of NO_x species [10,13]. High-resolution photoemission (U7A beamline) has been used to study the interactions of S_2, SO_2, NO, N_2O and NO_2 with a $TiO_2(110)$ surface [10,11,13,14]. Figure 1 shows the structural geometry of this surface. In a perfect

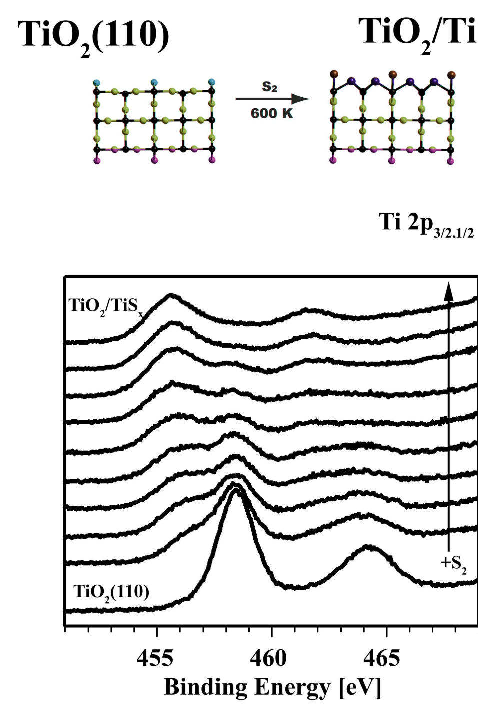

Figure 2. Ti 2p core level photoemission spectra for the reaction of sulfur with a $TiO_2(110)$ surface at 330 °C [11]. Photon energy= 625 eV

$TiO_2(110)$ surface, adsorbates can interact with pentacoordinated Ti sites (Ti_{pc}) or atoms in the O bridging rows (O_{br}). In addition O vacancies can be present in the O bridging rows or the bulk of the oxide sample [10,13]. Photoemission data and first-principles DF cal culations indicate that these vacancies play a dominant role in the chemical properties of the $TiO_2(110)$ surface [10,11,13]. When present on the surface they offer adsorption sites which are more reactive than Ti_{pc} or O_{br} sites [10,11,13]. Furthermore, *the exchange of O vacancies between the surface and bulk of the sample can lead to unexpected chemical transformations* [11,13]. Figure 2 shows Ti 2p core-level spectra for the adsorption of S_2 on $TiO_2(110)$ at 330 °C [11]. As sulfur is dosed, the peaks for TiO_2 completely disappear and new features appear for titanium sulfide. There is a complete $TiO_2 \rightarrow TiS_x$ transformation in the surface and near subsurface regions. This is surprising since oxides are much more stable than sulfides and a S_2(gas) + $TiO_2 \rightarrow$ TiS + SO_2(gas) reaction does not occur on the surface [11]. The key to the $TiO_2 \rightarrow TiS_x$ transformation is a S induced migration of O vacancies from the bulk of the oxide to the surface [11]. Adsorbates like Au and NO_x species can also induce a migration of O vacancies in TiO_2, thus producing an important enhancement in the chemical reactivity of this oxide surface [11-13].

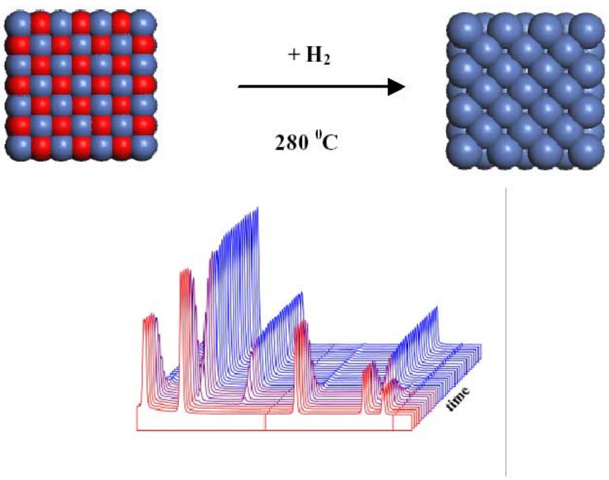

Figure 3. Time-resolved x-ray diffraction results for the reaction of a NiO powder with H_2 at 280 °C [14]. X axis is 2Θ, Y axis is time, and Z is intensity.

Reduction in Hydrogen and Activation of Oxide Catalysts

In most cases, pure stoichiometric oxides do not exhibit high catalytic activity [1]. One method frequently employed for the preparation of active oxide catalysts consists of partial reduction under hydrogen at elevated temperatures [1]. In this process, it is important to identify well-defined suboxides that can have high catalytic activity and are stable at the elevated temperatures typical of many catalytic reactions [1,11]. Experiments at beamline X7B have shown that *in situ* time-resolved x-ray diffraction is a powerful technique to study the reduction/activation of oxides [11,15]. Figure 3 displays time-resolved XRD data for the reaction of hydrogen with a NiO powder at 280 °C [14]. During the first 50 min, no major changes are seen in the intensity of the diffraction lines for NiO (in red). The NiO lines then begin to disappear, and simultaneously lines for metallic Ni appear (in blue), without any well-ordered intermediate phase. An induction or delay time was also found in photoemission experiments (U7A) for the reduction of a NiO(100) single-crystal, in NEXAFS/EXAFS

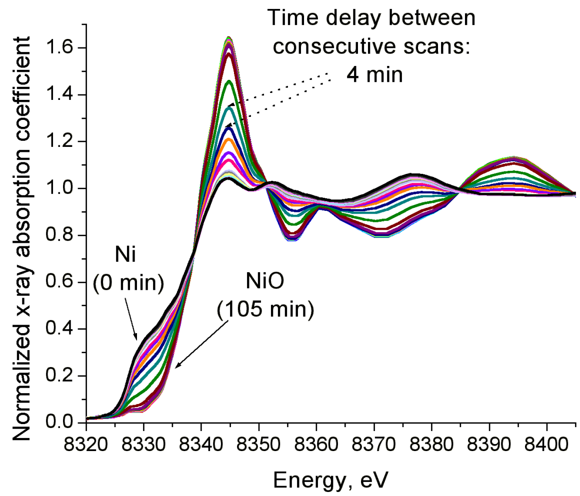

Figure 4. Time-resolved edge-step normalized NEXAFS data for the reduction of NiO powder at 280 °C under a flow of hydrogen [14].

measurements (X16C) for the reduction of NiO powder [14], and in time-resolved XRD data (X7B) for the reduction of cobalt and nickel molybdates [15]. Thus, such phenomenon must be taken into consideration when aiming at the activation of oxides via reduction in hydrogen.

In Figure 3, it could be argued that the induction time is associated with the formation of an amorphous NiO_x phase with special chemical properties. This possibility was ruled-out after analyzing NEXAFS/EXAFS data (Figure 4, for example) using the principal-component-analysis (PCA) method. The PCA results indicated that only two components (NiO initial phase, Ni final phase) were present in the system [14]. *Photoemission and DF results for the adsorption of H_2 on NiO(100) indicate that O vacancies play a key role during the induction time, generating the necessary sites for the dissociation of the adsorbate*. A perfect NiO(100) surface, the most common face of nickel oxide, exhibits a negligible reactivity towards H_2 [14].

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Tom Dickinson Retires

Bob Casey

Assoc. Chair for ESH&Q

It is important to note the retirement of Tom Dickinson from the NSLS on 12-21-2001. Tom has worked at the NSLS from its early days and contributed in so many important ways to the safety program. His perceptiveness, enthusiasm, and dedication will be sorely missed. Bill Thomlinson, the long-time NSLS Associate Chair for ESH at the NSLS, who now works at the ESRF, made the following comments in a letter to Tom sent just before his retirement:

"Your contributions extend far beyond the walls of BNL in our community of accelerators and synchrotron science. It is fair to say that I have not been in a synchrotron facility anywhere in the world where I do not feel your presence in the design, implementation and operation of safety systems, and safety operations in general. That is especially true here at the ESRF where the systems are modeled directly on those you so significantly helped to develop. I think that every facility built after NSLS, and those upgraded as well, use the system that we developed together with so many outstanding people at NSLS.

When we started with the development of the NSLS personnel protection systems, it was a green field cluttered with absolutely horrible examples at some of the other facilities. They were safe in their own ways since they effectively prevented anyone from doing any science. We took a different approach. You argued always and effectively for safety. I argued for efficient access to the experiments. It was then that the world of synchrotron research changed. We built a system that was, and is, efficient and inherently safe. We had to convince DOE that the efficient use of the beams by scientists was not counter to the principles of safety first. It was a tough sell, but we prevailed. The outstanding safety record at synchrotron facilities is the best testimony to our success.

Much more was at stake than building hardware. As I look back, your principal contribution was perhaps not the engineering of the hardware, but something far, far more important. For lack of better words, I will invent an oxymoron and say that you created a policy of "rigid flexibility". That may seem strange but what I mean is that you had a rigid approach, a no-compromise approach, to safety. But, at the same time, you also had a no-compromise approach to making sure that good science could be done if the proper safety concerns were addressed. You gained the utmost respect of the Users and often had to work one on one with them to assure that their experiments could go forward, but safely. A great deal of flexibility was, and is, required. That support by the User Community allowed us to go to NSLS, BNL and DOE with our ideas and in return we always had the full support of management. That was long before such things were popular. Because of that trust and support, we built systems and created operational principles that became the hallmark of synchrotron safety around the world."

I couldn't agree more with Bill's comments. The NSLS safety program has the stamp of Tom Dickinson in every fiber of its character, and it is widely recognized within the Laboratory and beyond as being uncommonly effective. I recently read the following comment made by a user at the end of his run at the NSLS: "I wish the rest of the Laboratory had the same common sense approach to safety that the NSLS does!" I can't think of a better tribute to the program that has had Tom at its center for the last 20 years.

Best wishes and good health to our colleague on his retirement. He will be missed!